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54 **Extruder process for preparation of carbon fiber reinforced fluoropolymer compositions.**

57 **An extruder process for blending carbon fiber and tetra-**  
**fluoroethylene copolymer resins, and laminates from the pro-**  
**duct of the process.**

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ACTORUM AG

TITLEEXTRUDER PROCESS FOR PREPARATION OF CARBON  
FIBER REINFORCED FLUOROPOLYMER COMPOSITIONSBACKGROUND

5 Carbon fiber reinforced melt-fabricable  
tetrafluoroethylene copolymer resins such as those  
disclosed in U.S. 4,163,742 issued August 7, 1979 on  
the application of Mansure, molded into such items as  
10 gaskets, valve seats, valve balls and various other  
compressor and pump parts, have displayed excellent  
resistance to deformation at high temperatures.  
These reinforced resins have heretofore been  
prepared, as taught by Mansure, by blending the resin  
and fibers in a mixture of water and a selected  
15 water-miscible organic solvent. This process,  
however, does not lend itself to acceptable  
continuous commercial production of the blended  
resin. It is, therefore, desirable to devise a more  
economical process for such production.

20 SUMMARY OF THE INVENTION

The subject invention is an extruder process  
for preparing a blend of carbon fiber and  
tetrafluoroethylene copolymer.

25 More specifically, in one embodiment of the  
subject invention, the process comprises providing a  
corotating, intermeshing twin screw extruder with a  
screw speed of 50 to 120 RPM, and a barrel  
temperature of 220 to 410 °C, said extruder having a  
first zone wherein the ratio of screw length to screw  
30 pitch is 11 to 15, a second zone for metering the  
blend and a die slot such that the slot opening is 2  
to 4 mm across; feeding the polymer and 20 to 35  
weight percent based on polymer of continuous carbon  
fiber into the first zone, therein melting the  
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polymer, chopping the fibers so that a substantial fraction is from 1.5 to 13 mm in length and blending the polymer and chopped fibers; and transferring the polymer/fiber blend through the second zone of the extruder and out of the extruder process through the die slot.

In another embodiment of the subject invention, the process comprises providing a corotating, intermeshing twin screw extruder with a screw speed of 50 to 120 RPM and a barrel temperature of 220 to 410 °C, said extruder having a first plasticating zone, a second zone wherein the ratio of screw length to screw pitch is 4 to 6 and a die slot zone such that the slot opening is 2 to 4 mm across; feeding the polymer into the first plasticating zone and retaining it therein until substantially molten; transferring the molten polymer to the second zone and concurrently feeding 20 to 35 weight percent based on polymer of continuous carbon fiber into said second zone whereby the fibers are chopped so that a substantial fraction is from 1.5 to 13 mm in length and blended with the molten polymer; and transferring the polymer/fiber blend out of the extruder through the die slot.

#### DETAILED DESCRIPTION

As in U.S. 4,163,742, the tetrafluoroethylene copolymer resins employed herein, in powder or pellet form, are melt-fabricable ones, as opposed to non-melt-fabricable resins typified by the homopolymer, polytetrafluoroethylene. Generally, polymers of the non-melt-fabricable variety have melt viscosities of  $1 \times 10^9$  poises or more at 380°C., whereas melt-fabricable tetrafluoroethylene copolymers have sufficient comonomer to lower the melt viscosity to  $1 \times 10^4$ - $1 \times 10^7$  poises at 380°C to

permit melt fabrication and still retain useful properties for fabricated articles.

Generally, the more comonomer present, the lower the melt viscosity. Thus, the melt-fabricable tetrafluoroethylene copolymers employed herein comprise copolymers of tetrafluoroethylene and, e.g., a different perfluorinated ethylenically unsaturated organic copolymerizable monomer present in an amount which allows the melt viscosity of the resultant copolymer to be below  $1 \times 10^7$  poise at 380°C. One preferred class of ethylenically unsaturated monomers is the perfluoro(alkyl vinyl ethers) of 3-7 carbon atoms. Generally, the copolymer can contain 0.5-20% by weight of these comonomers. Another preferred class is the perfluoro (terminally unsaturated olefins) of 3-7 carbon atoms. Generally, the copolymer can contain up to about 10-25% by weight of these comonomers. Other useful copolymers include those employing chlorotrifluoroethylene, as well as copolymers of tetrafluoroethylene and ethylene. If less than the amount of comonomer above specified is present, the copolymer described above will not be melt-fabricable; on the other hand, if more than the amount specified is present, the copolymer will become elastomeric.

The carbon fiber to be blended with any one of the above detailed resins will preferably have tensile strengths of at least 200,000 psi and a diameter of 2-20 microns, the surface of which being treated by conventional means, or optionally untreated. After chopping in accordance with the process of the subject invention, a substantial fraction of the fibers will have a length of between about 1.5 and 13 mm. The reinforced resin will contain 20 to 35 weight percent carbon fiber, and more preferably, 30 to 35 weight percent.



The process of the subject invention blends the tetrafluoroethylene copolymer resin and carbon fiber in a twin-screw, co-rotating, intermeshing extruder such as that designed by Werner and

5 Pfleiderer. For purposes of the subject invention, the barrel temperature should be such as will melt the tetrafluoroethylene copolymer resin, generally varying from about 220°C at the hopper to 410 °C at the die.

10 A critical aspect of the subject invention is the need to feed continuous carbon fiber into the extruder so that the fiber is chopped to the proper length and homogeneously blended with the then molten tetrafluoroethylene copolymer resin. If pre-chopped  
15 fiber is fed into the extruder, the fiber pieces tend to agglomerate by entanglement and will not feed uniformly into the extruder, hence, blending is impaired. For purposes of the subject invention, continuous carbon fiber is that having lengths at  
20 least about 10 cm so that the fiber is able to be wrapped around the extruder screw, thereby drawing the fiber uniformly into the extruder process. However, preferably, the continuous fibers are drawn into the extruder from a spool thereof.

25 In one embodiment of the subject invention, the continuous carbon fiber is fed, along with the tetrafluoroethylene copolymer resin, into the extruder at the hopper. In order to chop the fiber to the proper length, melt the resin and adequately  
30 blend the chopped fiber and resin, the first zone proximate the hopper need have a screw configuration such that the ratio of screw length to screw pitch is between about 11 and 15; a higher ratio will chop the fiber to less than the desired length and, therefore,  
35 compromise the reinforcing characteristics of the

fiber, while a lower ratio will fail to homogeneously blend fiber and resin. The screw speed useful for purposes of this particular embodiment should be between about 50 and 120 RPM.

5           Following this first zone, this embodiment of the process of the subject invention utilizes a conventional metering zone for transferring the blend to the extruder die, generally requiring a ratio of screw length to screw pitch of between about 2 and 9.

10           As another critical aspect of the subject invention, the die slot opening need be between 2 and 4 mm; a smaller opening tends to clog, while a larger opening does not align the fibers of the extruded sheet substantially in the plane of extrusion. Such  
15 fiber alignment results in expected compressive forces exerted on such articles to be perpendicular to the fibers, thus maximizing the fibers' reinforcing tendencies.

20           In another embodiment of the subject invention, the continuous carbon fiber is fed into the extruder through a vent port located downstream from the hopper. The tetrafluoroethylene copolymer is fed into the hopper, plasticated in a first zone of the extruder under conditions well known in the  
25 art, then transferred to a second zone wherein the vent port exists. This second zone need have a ratio of screw length to screw pitch of from about 4 to 6 in order to adequately chop the continuous fiber to be fed thereinto, and homogeneously blend this  
30 chopped fiber and resin. Again, a higher ratio will chop the fiber to less than the desired length, while a lower ratio will fail to homogeneously blend the fiber and resin. The screw speed useful for purposes of this particular embodiment should be between about  
35 50 and 120 RPM. After blending the chopped fiber and



resin, the blend is conveyed out of the extruder through a die slot, the particulars of such being detailed above.

The blend produced by the process of the subject invention exits the die slot in the form of a thin sheet. To form articles of substantial thickness, a plurality of these sheets can be laminated together in pressure molds well known in the art and detailed in the examples below.

#### Example 1

This example is to illustrate the embodiment of the subject invention wherein the continuous fiber is fed into the extruder, along with the resin, at the hopper.

A copolymer of tetrafluoroethylene perfluoro (propylvinyl) ether (about 3% alkyl ether and  $5 \times 10^{-4}$  poises at  $372^{\circ}\text{C}$ ) resin was fed at about 4 kg/hr into the hopper of a corotating twin screw, 28 mm Werner and Pfleiderer extruder with a screw speed of 112 RPM and a barrel temperature graduating from  $240^{\circ}\text{C}$  at the hopper to  $400^{\circ}\text{C}$  at the die.

Concurrently, continuous graphite fiber (Hercules "MAGNAMITE" AS with a diameter of 8 microns, a tensile strength of 2.8 GPa and a modulus of 0.22 TPa) was fed into the hopper at about 2 kg/hr, chopped and blended with the molten resin, and metered through the remainder of the extruder process. The screw configuration was as follows:

	extruder length (mm)	screw pitch
	0	
	90	
	180	45 (triple flight)
	270	
	360	
	450	
	540	
	630	
	720	30 (single flight)
	780	

so that the ratio of screw length to screw pitch in the first zone, i.e., the first 540 mm, was 12, and the ratio in the second metering zone was 2.7. (In calculating screw length to screw pitch ratios, a triple flight screw was used as the standard, therefore, when the ratio is calculated for a configuration containing a single flight screw element, the ratio for that particular element need be divided by 3 before adding the ratio for that element to the ratios of the remaining triple flight elements). The blend was metered out of a 2.3 mm die slot opening in sheet form. Sheet disks were cut to 8.6 cm in diameter and a total of 170 g loaded into a laminating pressure mold (conventional cross-lamination being preferred). The mold was then placed in a press and heated under contact pressure to 345°C, held for 15 minutes under about 7 MPa pressure (4536 kg force), cooled to room temperature under pressure and removed from the mold. The percent deformation at 235°C (ASTM D621, 24 hr deformation under 14 MPa pressure) was measured at 1.3.

#### Example II

This example is to illustrate the embodiment of the subject invention wherein the continuous fiber is fed into the vent port of the extruder.

The resin used in Example I was fed into the hopper of the same extruder at about 3 kg/hr and melted in the first zone of the extruder. The screw speed was 110 RPM and the barrel temperature graduated from 225°C at the hopper to 402°C at the die. The molten polymer was passed into a second zone having a vent port therewith while continuous graphite fiber was fed at about 1.0 kg/hr into the extruder through this vent port. The screw configuration was as follows:



	extruder length (mm)	screw pitch
	0	
	30	
	60	45 (triple flight)
5	90	
	120	
	150	
	180	
	(first zone) 210	30 (triple flight)
	240	
10		<u>24</u> (triple flight)
	270	left hand kneading block
	300	
	330	<u>24</u> (reverse)
	360	
	390	45 (triple flight)
15	420	
	450	
		<u>30</u> (triple flight)
	480	<u>24</u> (reverse)
	510	<u>45</u> (triple flight)
	540	(vent port)
20	570	30 (single flight)
	(second zone) 600	
	630	
	660	
	690	45 (triple flight)
	720	
	750	
25	780	<u>30</u> (triple flight)

so that the first zone is a conventional plasticating zone and the second zone containing the vent port has a screw length to screw pitch ratio of 3.0. As the fiber entered the extruder, it was chopped and blended with the molten resin, the blend then metered out of the extruder process through the die slot as detailed above. Again, also detailed above, sheets exiting the die were laminated and percent deformation measured as 0.8 at 200°C and 1.0 at 235°C.

Delamination Valve Test

5 A laminate prepared in accordance with the  
procedure of Example I was cut in the shape of a  
conventional valve seat and subjected to 15,000  
cycles in a Worcester ball valve in a 170°C (0.7 MPa)  
steam line. After cycling, the valve seat continued  
to hold 4.5 MPa hydrostatic pressure.

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CLAIMS

1. A process for preparing a blend of a melt-extrudable tetrafluoroethylene copolymer and carbon fiber comprising:

- 5 (i) providing a corotating, intermeshing twin screw extruder with a screw speed of 50 to 120 RPM, a barrel temperature of 220 to 410 °C, a first zone wherein the ratio of screw length to screw pitch is about 11 to 15, a second zone for metering the blend and a die slot having an opening of 2 to 4 mm;
- 10 (ii) feeding the polymer and 20 to 35 weight percent based on polymer of continuous carbon fiber into the first zone, therein melting the polymer, chopping the fibers so that a substantial fraction is from about 1.5 to 13 mm in length and blending the polymer and chopped fibers; and
- 15 (iii) transferring the polymer/fiber blend through the second zone of the extruder and out of the extruder process through the die slot.
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2. A process for preparing a blend of a melt-extrudable tetrafluoroethylene copolymer and carbon fiber comprising:

- 25 (i) providing a corotating, intermeshing twin screw extruder with a screw speed of 50 to 120 RPM, a barrel temperature of 220 to 410 °C, a first plasticating zone, a second zone wherein the ratio of screw length to screw pitch is 4 to 6 and a die slot having an opening of 2 to 4 mm;
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(ii) feeding the polymer into the first plasticating zone and retaining it therein until substantially molten;

5 (iii) transferring the molten polymer to the second zone and concurrently feeding 20 to 35 weight percent based on polymer of continuous carbon fiber into said second zone whereby the fibers are chopped so that a substantial fraction is from about 1.5 to  
10 13 mm in length and blended with the molten polymer; and

(iv) transferring the polymer/fiber blend out of the extruder through the die slot.

15 3. The product of the process of Claim 1 or Claim 2. the process of

4. The product of Claim 1 or 2 in the form of a laminate.

5. A shaped article formed from the  
20 laminate of Claim 4.

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# EUROPEAN SEARCH REPORT

0086639

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 83300697.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	EP - A1 - 0 026 806 (PAMPUS) * Claims; page 5, line 10 - page 7, line 18 *	1,3	C 08 J 3/20 C 08 F 14/26 C 08 K 7/06 C 08 L 27/18
D,A	US - A - 4 163 742 (J.F. MANSURE) * Column 1, line 43 - column 2, line 50; claims *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 08 J C 08 L 27/00 C 08 K C 08 F 14/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 20-05-1983	Examiner TENGLER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background () : non-written disclosure I* : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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